

**Washington State Toxics Monitoring
Program:
Exploratory Monitoring of Toxic
Contaminants in
Edible Fish Tissue and Freshwater
Environments of Washington State**

Quality Assurance Project Plan

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Background

Toxic contamination of our air, water, and soil is a concern for the health of the public and provides some of the greatest challenges to environmental managers. These contaminants include polychlorinated biphenyls (PCBs), chlorinated pesticides, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-p-furans (PCDD/Fs), and mercury. Many of these chemicals are persistent, they do not break down easily and remain in the environment for decades. Many toxic contaminants also bioaccumulate; their concentrations in organisms increasing at the higher trophic levels because the contaminant is not broken down or excreted by metabolic processes. The accumulation of these chemicals can have a variety of health effects on humans and wildlife such as reproductive abnormalities, neurological problems, and behavioral changes.

Monitoring efforts in Washington State have detected toxic contaminants in surface water, sediment, and aquatic animal tissues. In many studies, concentrations of toxic contaminants in water, sediment, and tissue have been high enough to threaten the health of humans, wildlife, and fish. Resource management decisions resulting from toxic contamination have included establishing fish consumption advisories, Clean Water Act Section 303(d) listings of contaminated waterways, the regulation of fertilizers, and contaminant source identification and control. The Washington State Department of Health (Health) currently has ten fish consumption advisories in Washington State due to contamination by mercury, PCBs, PCDD/Fs, chlorinated pesticides, and /or other metals and organic chemicals. Three consumption advisories exist for shellfish due to similar contaminants (Health, 2001).

Ecology has conducted or participated in studies that characterized toxic contaminants in Washington. The Washington State Pesticide Monitoring Program (WSPMP) monitored surface water, fish, shellfish, and sediments throughout the state from 1992 to 1997 in areas suspected of contamination (Davis, 2000). The Puget Sound Ambient Monitoring Program (PSAMP) monitors toxic contaminants in sediments and fish throughout Puget Sound with Ecology participating in several components of this program (Llanso, et al., 1998). Ecology has conducted numerous studies for site-specific concerns in freshwater environments (such as those associated with point source discharges) as well as for streams and lakes on a statewide basis (Johnson and Norton, 1990; Hopkins, 1991; and Serdar, et al., 1994). Fish tissue and sediment from several areas throughout Washington are contaminated with PCDD/Fs and Yake, et al. (1988) characterized sources of these contaminants in Washington. Johnson and Olson (2001) described the occurrence of PBDEs in Washington fish; these compounds were previously unreported in Pacific Northwest fish.

A number of agencies other than Ecology have contributed to our knowledge of toxic contaminants in Washington. The U. S. Geological Survey (USGS) has monitored pesticides in several Washington basins as part of their National Water-Quality Assessment Program (NAWQA). Watersheds that are NAWQA projects include: Central Columbia Plateau, Yakima River, and Puget Sound (Williamson, et al., 1998; Rinella, et al., 1993; MacCoy and Black, 1998; Bortleson and Ebbert, 2000). The U.S. Environmental Protection Agency (EPA)

monitored fish tissue during the mid-1990s for toxic contaminants as part of the Columbia River Basin Fish Contaminant Survey (CRITFC) (EVS, 2000). EPA is also conducting a National Lakes Study which characterizes toxic contaminants in lakes throughout the nation; Ecology participates by conducting field collection of fish (Tetra Tech, 2000). The U.S. Fish and Wildlife Service (USFWS) sampled for toxic compounds in the 1980's during the National Contaminant Biomonitoring Program (Schmitt and Brumbaugh, 1990; Schmitt, et al., 1990).

While site-specific monitoring has occurred and continues to occur in Washington State for specific concerns, a broad and consistent statewide toxics monitoring effort has not been developed. Efforts to monitor toxic contamination in fish tissue, sediments, water, and wildlife in Washington on a programmatic basis have declined during the last decade since funding for the WSPMP ended. Interest in toxic contamination of our water, fish, and wildlife was rekindled in 2000 and Ecology management directed resources to the development of a Washington State Toxics Monitoring Program (WSTMP). A technical committee of Ecology staff reviewed issues surrounding toxics contamination in Washington and developed a conceptual base for toxics monitoring (Yake, 2001). While a range of concerns and issues were discussed, limited resources resulted in the selection of four components for the initial Washington State Toxics Monitoring Program:

- Conduct exploratory monitoring to identify new instances and locations of toxics contamination in freshwater environments and freshwater fish tissue.
- Conduct trend monitoring for persistent toxic contaminants using residues in edible fish tissue.
- Establish an Internet Web page featuring toxics monitoring efforts in Washington to disseminate and inform citizens about toxics contamination.
- Develop other toxics monitoring efforts to address particular issues and establish cooperative programs with other agencies.

This Quality Assurance Project Plan (QAPP) addresses the first component (exploratory monitoring) listed above. This QAPP was prepared following guidance developed by Lombard and Kirchmer (2001).

Problem Statement

Humans and wildlife face a variety of risks due to toxic chemicals in the environment. For many areas of Washington, information is lacking about the levels of toxic contamination in freshwater fish and surface water.

Project Description

Goal

The goal of this project is to investigate the occurrence and concentrations of toxic contaminants in edible fish tissue and surface waters from freshwater environments in Washington where contamination is suspected yet recent data are absent.

Objectives

- Provide information about the level of toxic contamination in surface water and edible fish tissue from freshwater lakes, rivers, and streams that have not yet been monitored or where relevant data are greater than ten years old.
- Provide a screening level assessment of the potential for adverse effects of toxic chemicals on aquatic biota and other wildlife.
- Provide screening level information to the Washington State Department of Health that could be used to trigger additional studies for evaluating health risks associated with the consumption of fish.
- Provide information for resource managers and the public about the status of toxics contamination in water and edible fish from freshwater environments in Washington.

Project Organization and Schedule

Organization

All persons listed below work within Ecology's Environmental Assessment Program at Olympia, Washington.

Keith Seiders

Overall project manager on the exploratory monitoring component. Develops QAPP, organizes and conducts field sampling efforts, arranges laboratory analysis, and develops annual report. Phone 360-407-6689.

Bill Yake

Provides conceptual and technical guidance on development of the exploratory monitoring component, reviews QAPP, assists with field sampling, and assists in report development and review. Phone 360-407-6778.

Dale Norton

Oversees component management and budget, provides conceptual and technical guidance, reviews/approves QAPP, and reviews reports. Phone 360-407-6765.

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Reviews/approves QAPP and provides guidance on analytical methodology and data quality. Phone 360-407-6455.

Stuart Magoon

Coordinates laboratory services (i.e. sample analyses, data quality documentation, data submittal to EIM), data quality reviews, and provides guidance on analytical methodology and data quality. Phone 360-871-8801.

Will Kendra

Reviews/approves QAPP and reviews reports. Phone 360-407-6698.

Morgan Roose, Randy Coots, and Dave Serdar

Assists with field sampling. Phone 360-407-6458, 360-407-6690, and 360-407-6772, respectively.

Art Johnson and Mike Gallagher

Reviews and comments on QAPP. Phone 360-407-6766 and 360-407-6868.

Schedule

This schedule is for the initial year. The completion of tasks in subsequent years would occur during the indicated month for a given year.

Fish Tissue (Includes Water Samples Collected Concurrent with Fish Collection)

Sample Collection	October - November, 2001
Tissue Processing	November - December, 2001
Laboratory Analyses	December, 2001 - January, 2002
Laboratory Data to Project Officer	February - March, 2002
Data Entry in EIM	March, 2002
Draft Annual Report	May, 2002
Final Annual Report	June, 2002
Site Selection for Following Year	July, 2002

Water (For Spring/Summer 3x Repetitive Sampling Effort)

Sample Collection	April - July, 2002 (3x/site)
Laboratory Analyses	May - August, 2002
Laboratory Data to Project Officer	September - October, 2002
Data Entry in EIM	November, 2002
Draft Report	January, 2003
Final Report	March, 2003
Site Selection for Following Year	April, 2003

Sampling Design

Sampling Strategy

Fish Tissue

Fish tissue samples will be collected from selected sites throughout the state. Collection of target fish species will occur annually during the late summer to early fall (September-October) since lipids content is usually higher at this time; lipids are where organic contaminants tend to be stored in organisms. Water levels are also lowest at this time, allowing easier and safer access. One to two species of fish will be collected at each site, with five to ten fish of each species forming a composite sample as recommended by EPA's Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories (EPA, 2000). Ten fish will be the target number for a composite sample; no less than five fish will be used in a single composite. Individuals used in a composite sample should:

- Satisfy any legal requirements of harvestable size or weight, as defined by the Washington State Department of Fish and Wildlife (WDFW) in their sport fishing rules, or at least be of consumable size if no legal harvest requirements are in effect.
- Be of similar size so that the smallest individual in a composite is no less than 75 percent of the total length of the largest individual.
- Be collected within a two-week period. (It may take more than one day to capture adequate numbers of fish from a site).

Fish will be collected using methods most appropriate for the target species and site characteristics. The primary method will be electrofishing using a boat or backpack units. Other methods may be used where electrofishing is impractical. In these cases, hook and line or the use of nets (gill net, trawl net, fyke net) may be employed. Collection methods will be used that minimize unintended capture of non-target fish. When adequate species or numbers of fish are not available from a preferred site, an alternative site will be selected for sampling.

Water

Water sampling will address two objectives: to characterize pesticides concentrations in water where fish tissue sampling occurs; and to characterize pesticide concentrations during times of pesticide application in urban and agricultural settings. At sites selected for fish tissue sampling, water samples will be collected from a well-mixed area of the waterbody (when available) prior to fish collection. Urban and agricultural sites will be sampled three times during the spring and summer during the pesticide application season. Information about pesticide use in selected basins will be obtained by consulting with persons knowledgeable about local practices, such as Conservation District and Cooperative Extension staff.

Water samples will be composites to better represent the waterbody being sampled. For streams, the composite will consist of subsamples taken from horizontal and vertical transects of the stream. For lakes, depth-integrated subsamples will be taken from one or more locations in the lake and then composited. Detailed descriptions of water sampling methods are described in the section on Field Procedures.

Representativeness

Site Selection for Fish Tissue

Fish tissue data collected in Washington by Ecology, EPA, USGS, and USFWS were reviewed to determine the nature of past monitoring efforts. More than 200 sites have been sampled for analysis of fish tissue since about 1980. The type of tissue, species, and analytes varied among the many monitoring efforts.

About half of the available data was compiled in summary tables that included site locations, tissue types, and parameters analyzed. These sites were then displayed using ArcView GIS to examine the location and nature of current information on fish tissue. Areas that are on the state's 1998 303(d) list for contaminants in fish tissue will not be sampled in this program for listed contaminants because these sites are likely to be sampled during Total Maximum Daily Load (TMDL) studies. Where data used for listing a waterbody are more than ten years old, the waterbody may be considered for sampling during this effort.

Potential sampling sites were selected after considering factors related to the probability of site contamination and the nature of the fish resource. The presence of public fishing opportunities and the nature and age of historical fish tissue sampling efforts guided the initial selection of sites. Locations of many potential pollution sources were identified using Ecology's Facility/Site database (Ecology, 2001) with ArcView GIS. The Washington Atlas and Gazetteer (DeLorme Mapping, 1988) was also used to help evaluate the proximity of potential sources of contamination. Sample site selection will occur each year using a similar process and consider new information and concerns. Factors considered in site selection include:

Probability of Detecting Contamination in Areas Not Previously Monitored

- Suspected contamination due to the proximity of historic or current land uses such as: pesticide handling/storage, pesticide application as in agricultural areas, wood treating facilities, EPA Superfund sites, metal ore processors, pulp mills, refineries, chemical handlers, incinerators, and coal-fired power plants.
- Lack of recent (within the last 10 years) data on levels of toxic contaminants in fish tissue.

Value and Interest of the Fish Resource to Consumers

- Popularity of sites by the fishing public and/or high consumption rates by the public; value or interest of the site as indicated by the experience of various Ecology staff.
- Ability to collect appropriate fish considering: site accessibility for sampling, presence of adequate fish age and size classes, ability to capture fish, and the bioaccumulative characteristics of target analytes among species present.

Several sites that are suspected of having no contamination were also chosen in order to gain some perspective on the results from sites suspected of contamination. The criteria for such “reference” sites are the same as those listed above except the probability of detecting contamination is low. These sites would be streams and lakes far from potential sources or contaminant transport mechanisms.

About 100 sites were initially screened using this process which resulted in candidate sites for the first year of sampling (Figure 1). First-year candidate and alternate sites are listed in Appendix A-1 along with target analyte groups and rationale for selection. A regional distribution of selected sites was desirable in order to address toxic contamination as a statewide concern. Because federal scientific collection permits (discussed below) for this study may not be available until July 2002, this first year’s effort is restricted to sites where federal permits are not required.

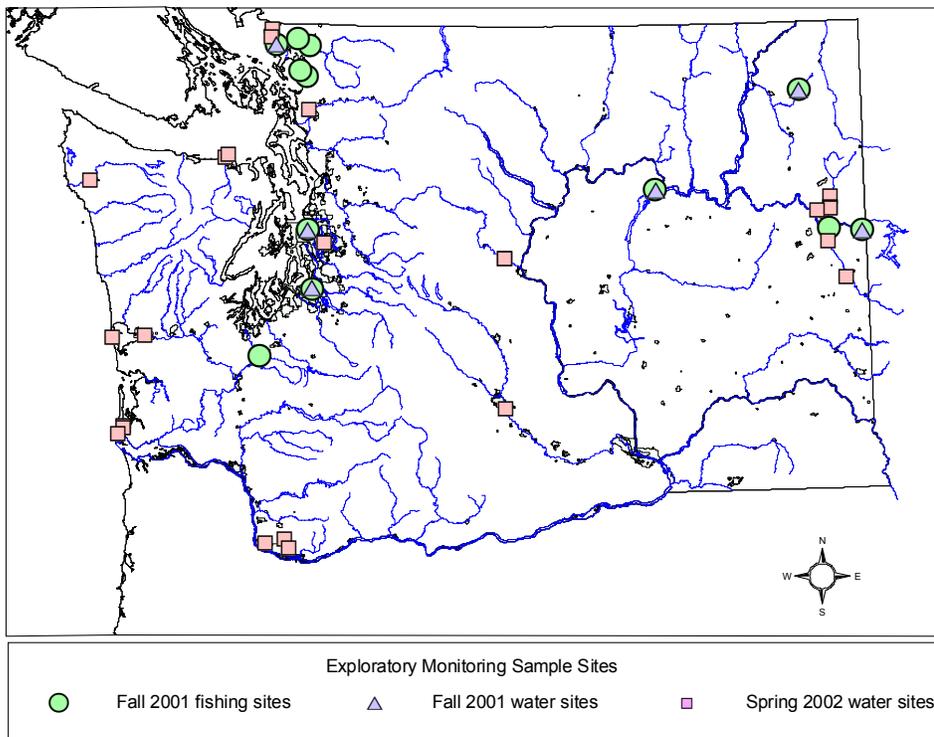


Figure 1. Proposed Sample Sites for 2001-2002

A number of variables were considered in determining the suitability of a site for fish collection such as: types of species present, location and regional distribution, suite of target analytes for that site and species, analytical budget, need for scientific collection permits from federal and state agencies, site accessibility, and likelihood of success in catching target species. The rationale for selecting individual sites is noted in Appendix A-1 and demonstrates that many sites are grouped roughly by geographic location and conditions they may be representative of. For example, five or more sites are located in the Federal Way area, and only one of these sites would be selected. The designation of multiple target sites contributes to flexibility in selecting sites as circumstances change during the progression of field work. Estimates of analytical costs for samples from one or two species at selected sites are listed in Appendix A-1.

Biologists from WDFW will be contacted to better determine the nature of the fishery and fish stocks at candidate sites. Factors needing consideration prior to sampling include: fish size and age classes present, fish stocking practices, length of time target species reside at the candidate site, popularity of the site to the public, and ease of fish capture. Many of Washington's lakes and streams contain fish that originate from natural and hatchery production. There may be sites where hatchery fish of significant size are planted for upcoming fishing seasons. These hatchery fish may bioaccumulate different amounts of contaminants than do naturally produced fish because of differences in the time these fish are exposed to contaminants.

Site Selection for Water

Sites for water sampling will be selected to address two objectives: characterize pesticide concentrations in water where fish tissue sampling occurs and characterize pesticide concentrations during times of pesticide application in urban and agricultural settings. Sites selected for the urban and agricultural characterization will include a mix of sites: those that were monitored in previous studies, those which previous studies recommended for monitoring, and those where no data exist. Site selection for water sampling will use a similar process as that previously described for fish tissue site selection. Information from historical sampling efforts will be compiled, reviewed, and then used to help select sites for monitoring. Criteria for selecting sites for spring-summer monitoring include:

- Presence of potential sources of contamination and contaminant transport mechanisms.
- Probability of detecting target analytes considering factors such as basin size and flow.
- The site is not listed in the State's 1998 303(d) list for analytes of interest (listed waters are anticipated to be studied during the TMDL process).
- The area or site has been recommended for monitoring from previous studies.
- For new sites, previous monitoring data are lacking.
- For sites previously monitored, historical data are sparse (data greater than ten years old).
- The site may be within the drainage basin where fish have been collected for tissue sampling.

As with sites for fish collection, a regional distribution of selected sites is desirable in order to address toxic contamination as a statewide concern. Also, one or more "reference" sites may be selected to help provide perspective on findings from other sites. These sites would be streams and lakes far from potential sources or contaminant transport mechanisms. The number of sites to be monitored will largely be determined by resources available for collection and analysis of

samples. Initially, eight sites from a list of potential sites (Appendix A-2) will be selected for the spring-summer repetitive sampling while approximately five sites will coincide with fish tissue collection (Figure 1).

Target Analytes for Fish Tissue and Water

Target analytes for fish include various persistent, bioaccumulative, and toxic chemicals that have been found in water, sediments, and fish tissue in other monitoring efforts in Washington. Most sites will be sampled for a basic suite of contaminants: chlorinated pesticides, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and mercury. The lipid content of tissue will be determined as an ancillary parameter. Other analytes may be added when site characteristics warrant. For example, PCDD/Fs are of interest at some sites due to the proximity of potential sources. A different Ecology study will be looking at levels of total and inorganic arsenic in fish tissue from Washington so this project will not include arsenic as a target analyte.

Target analytes for water include a broad number of pesticides. For sites where fish tissue is collected, about 50 chlorinated pesticides are the target analytes for water samples. For the urban and agriculture repetitive sampling sites, about 140 analytes are targeted and include pesticides from the chlorinated, organophosphorus, nitrogen, and carbamate groups. Ancillary parameters for water samples include lab determination of total organic carbon (TOC) and total suspended solids (TSS). Field measurements will include temperature, conductivity, and pH. Streamflow may be measured or determined from other sources such as USGS. Target analytes for fish tissue and water are listed in Appendix B.

Target Fish Species

Target species were selected based on recommendations from EPA (2000) and previous experience with fish collection efforts in Washington. The following criteria were used to select target species:

- Are commonly captured and likely to be consumed by humans.
- Potentially bioaccumulate high concentrations of chemicals of interest.
- Abundant, easy to identify, and easy to capture.
- Large enough to provide adequate tissue for analysis.
- Resident fish and fish likely to stay relatively close to the sampling site.

Target species for this study are listed in Appendix C. Efforts will focus on collecting the desired species and number of fish, yet the outcome of field sampling will depend on the availability and abundance of fish at the study sites. In some cases, two different species may be sought due to differences among species to bioaccumulate certain types of chemicals. While edible game fish are preferred over bottom-dwelling species, bottom feeders in some areas that are caught and consumed by humans may also be collected. Information about managed species at sites will be obtained from WDFW biologists.

Comparability

Data from this project will be compared to various regulatory and/or biological effects concentrations, as well as findings from historical work. Sample collection, processing, and analytical methods used will be documented and are expected to produce data that are comparable to various criteria and data from other studies. Data regarding the lipid content and tissue type from this study will help to allow appropriate comparisons to be made. Monitoring results may be compared to various standards and previous studies such as:

- Criteria in Washington's water quality standards (Chapter 173-201A WAC) and the National Toxics Rule (40 CFR 131).
- Results from historical work in Washington, such as from WSPMP and NAWQA.
- Risk-based consumption values as described in EPA (2000).

Data Quality Objectives

The quality of analytical data will be evaluated according to MEL's practices described in Ecology's Lab User's Manual (Ecology, 2000). The data review process is an integral part of producing analytical results at MEL. This review addresses: sample preparation, instrument calibration and performance, completeness of the raw data package, checks for errors, holding times, and usefulness of the data. These reviews are summarized in a case narrative that accompanies the reported results.

The case narratives and field data will be reviewed by the project officer to determine how the data compare to the Measurement Quality Objectives (MQOs) for this project. The MQOs were developed using information about data quality from past monitoring efforts of fish tissue and water (Davis, 1998; Davis, et al., 1998; and Serdar, et al., 1999). Appendix D contains MQOs for: practical quantitation limits, bias, precision, and accuracy for target analytes. Data quality assessment will be made using information from laboratory case narratives, laboratory duplicates, field replicates, matrix spike recoveries, and matrix spike duplicate recoveries.

Field Procedures

Sampling Procedures

Scientific Collection Permits

Scientific collection permits will be acquired prior to collecting fish. Washington's Department of Fish and Wildlife issues permits for any collection activities in the state. For areas inhabited by fish listed under the Endangered Species Act (ESA), the appropriate permit will be obtained from National Marine Fisheries Service (for anadromous species) or the U.S. Fish and Wildlife Service (for inland species). Approximately three to six months are needed for these federal

agencies to process applications for scientific collection permits. Permits are expected to be issued in the summer of 2002 and be valid for up to five years.

Permits are needed because ESA-listed species may be encountered during collection activities. The collection methods used (electrofishing primarily) may disturb or harass listed species and is considered “take” under the ESA. There are currently 15 species or stocks of anadromous fish in Washington waters that are listed or are proposed for listing as endangered or threatened. The Bull Trout (*Salvelinius confluentes*) is listed as threatened in Washington and other northwest states. These species or stocks collectively inhabit large areas of Washington so the initial year’s collection efforts will focus on areas where federal collection permits are not needed.

Fish Tissue

Methods for the collection, handling, and processing of fish tissue samples for analysis will be guided by methods described in EPA (2000). Upon capture in the field, fish will be identified to species and target species retained: non-target species will be released. Fish that are retained will be inspected to ensure that they are acceptable for further processing (e.g. proper size, no obvious damage to tissues, skin intact). Fish to be kept will be stunned by a blow to the head with a dull object, rinsed in ambient water to remove foreign material from their exterior, weighed, and their fork and total length measured. Individual fish will then be double-wrapped in foil and placed in a plastic zip-lock bag along with a sample identification tag. The bagged specimens will be placed on ice in the field. Fish may remain on ice for a maximum of 24-48 hours and then they will be frozen to -20 C at Ecology facilities in Lacey, Washington. Sampling instructions for field crews are given in Appendix E.

Up to ten fish will be used to create a composite sample for laboratory analyses. The edible portion of target species will be used for the composite sample. Fish will be removed from the freezer and partially thawed; and then, in most cases, filleted. Whole fish and/or other tissues may be used in cases where people prepare fish using more than muscle tissue. Gamefish fillets will include the skin and belly flap. Skin will be removed from scaleless fishes (e.g., catfishes) and fish to be analyzed for mercury (e.g. largemouth bass) prior to filleting. Appropriate structures used to determine the age of individual fish (scales, otoliths, opercles, spines) will be extracted and sent to a WDFW biologist contracted to determine fish age from these structures.

Fillets for compositing will be cut into small cubes, and equal weights from each individual fed into a grinder or blender in order to yield a composite sample of adequate size for the required analyses. The ground tissue will be homogenized by stirring to a consistent texture and color. Subsamples from the homogenate will be taken and placed into appropriate containers and transported to the laboratory for analyses. Excess homogenate will be placed into an appropriate container, labeled, and archived frozen at -20 C .

Water

Water samples for organic contaminant analyses will be collected following procedures described by Davis (1993) for the WSPMP. For streams, depth-integrating samplers will be used at three points along a stream cross section to obtain a sample representative of the stream.

Samples from each point will be composited to obtain adequate volume for the analyses to be requested. Several models of USGS depth integrating samplers and nozzles will be used depending upon water depth, stream velocity, and ease of handling. These samplers use Teflon™ and glass for the parts of the device that contact sample water. A DH-76 sampler, attached to a cable or rope, is available for use from bridges where the water is swift and deep. A DH-48 sampler, attached to a wading rod, is available for use in waters with velocities less than four feet per second and up to four feet deep. Hand grab samples will be taken where waters are less than one foot deep.

The sample collection methods for lakes and reservoirs will depend upon the characteristics of the waterbody and use techniques described by Rogowski and Davis (1999) when possible. For small lakes, one location will be selected for sampling while two or three locations on larger lakes may be selected for sampling. Sites that are believed to be representative of the lake will be chosen.

For shallow lakes that are not stratified (as determined by a vertical temperature profile) samples will be collected with a DH-76 sampler attached to a depth-marked hand line. The depth of the water will first be determined using the sampling vessel's depth sounding device or a marked and weighted line. The amount of line that the sampler can be lowered to, within several feet of the bottom, will be measured and marked. The sampler will then be lowered at a constant rate to the marked depth and then raised at a constant rate. The rate of lowering and raising will be adjusted in order to allow the sample container to just fill as it is recovered from the water. Upon recovery, the water sample will be transferred to an appropriate sample container. This process will be repeated until the desired sample volume is collected.

For deep lakes, water will be collected from several depths within the epilimnion and the hypolimnion. A sampling device such as General Oceanics' "Go-Flo" will be rinsed in surface water, lowered to desired depths, and triggered to collect a sample. The sampler will be retrieved and the desired volume of water sample will be transferred to a sample container. This process will be repeated until the desired depths have been sampled and an adequate sample composited. The final sample will consist of equal volumes from each of the two to six depths sampled. The parts of the sampling device that contact the sample are made with stainless steel and/or Teflon™; these areas will be decontaminated as described below for each waterbody the sampler is used at.

Decontamination Procedures

All utensils used for processing tissue samples will be cleaned in order to prevent contamination of the sample. Utensils include bowls and knives of stainless steel and tissue grinding appliances having plastic and stainless steel parts. All utensils for fish tissue sampling will be cleaned with the following procedure: soap (Liquinox) and hot water wash; hot tap water rinse; deionized water rinse; and a final rinse with pesticide-grade acetone, hexane, and/or methanol (choice of solvent depending upon the exact materials used in sampling or processing equipment). Utensils will be air-dried and then packaged in aluminum foil until used. Water sampling devices will be

cleaned and packaged in the same way. Fish will be filleted and tissues processed on aluminum foil that covers the workbench.

Field Records

Field notes will be kept for each sampling event. Notes will be entered in a field notebook and include: date and time, sampling personnel, general sampling location and latitude/longitude coordinates of fish collection, general weather conditions, method of sampling, fish species collected, weights and lengths for individual specimens, and results from field measurements. Latitude and longitude coordinates, and their datum, will be obtained with a state-of-the-art, hand-held Global Positioning System (GPS) device. Additional notes will be taken when samples are processed and submitted for laboratory analysis such as: type of tissue, laboratory identification numbers, and laboratory analyses requested. The sex of individual fish will be determined during tissue processing.

Sample Handling

Containers and Preservation

Tissue and water samples will be stored, preserved, and transported following procedures designed to maintain the integrity, quality, and identification of the sample. Appendix F includes requirements for sample containers, preservation, and holding times for each set of analyses required for tissue and water. Pre-cleaned sample containers will be obtained prior to field sampling efforts with containers for metals and organics possessing Quality Assurance Certification from the supplier (e.g. I-Chem 200 series or equivalent).

Identification and Transport

The identification of water and tissue samples will be maintained from the time of collection to the time of reporting of results. For water samples, the sample container will be tagged and labeled with a unique laboratory identifier. A field record form will be created to record information about the sample collected: location, date, time, and the method of collection. Other information may also be recorded on the field form – such as observations about land use.

For tissue samples, a field record form will be created for describing individual fish and their attributes such as: species, length, weight, site location, date of capture, and any other observations. Field record forms will be patterned after examples given by EPA (2000) and clearly identify the laboratory identifier code used for each sample. Whole fish will be transported, on ice, to Ecology headquarters facilities in Lacey, Washington by field crews. Fish will be frozen to -20 C at the Ecology facility until processed at a later date.

Fish samples will be processed (tissue removed, composited, and homogenized) and then put into the appropriate sample containers for transport to the laboratory. Sample containers will be tagged and labeled with unique laboratory identifier. These numeric and alphanumeric

identifiers will be in the format used by Ecology's laboratory and data management systems. Ecology's "Request for Analysis" form will accompany the samples transported to the laboratory. This form includes sample information such as: date and time of collection, numeric and alphanumeric identification codes, sample media, number of containers, analyses requested, and a chain-of-custody record. The laboratory will be notified of the approximate date when samples will arrive for analysis. The type of structures removed for determining the age of individual fish will be noted, assigned an identification number, and packaged for shipment to WDFW for aging. Containers for these structures will be supplied by WDFW.

Laboratory Procedures

The analytical methods for target analytes were selected to achieve a balance of analytical sensitivity, comparability, and cost-effectiveness. Appendix F summarizes the parameter groups to be analyzed for, sample matrix, analytical method, practical quantitation limits (PQL), sample containers, preservations, and holding times for samples. The laboratory procedures to be used by the Ecology/EPA Manchester Environmental Laboratory (MEL) are documented in Ecology (2000).

Appendix G shows the desired PQLs for individual analytes. Unfortunately, the PQLs for a number of analytes are higher than criteria found in water quality standards or screening level criteria. For tissue samples, these analytes include toxaphene, total PCBs, and PCDD/Fs. For water samples, the freshwater chronic criteria in Washington's water quality standards (Chapter 170-201A WAC) are lower than the selected method's quantitation limits for: DDT and metabolites, chlordanes and nonachlors, aldrin and dieldren, endrin, heptachlor, heptachlor epoxide, and toxaphene. Values in bold in Appendix G are desired PQLs that may not be met using the selected analytical methods: the bold value approximates the value of the water quality criterion or screening level for fish consumption for the specific analyte.

The EPA (2000) recognizes the unavailability of cost-effective analytical methods that can achieve lower quantitation limits for some analytes. The use of performance-based analytical techniques are encouraged by EPA which may help in developing analytical methods that achieve needed detection limits for particular analytes. This project anticipates that method development will occur in other studies where method development is the focus and that those methods can be incorporated into this study as they become available. For example, MEL is exploring the use of larger sample volumes for use in gas chromatography; the goal is to lower detection limits for some chlorinated pesticides and PCBs for a water quality study in the Walla Walla River basin (Johnson, 2002; Mandjikov, 2002).

Appendix H shows estimated analytical costs for one year's analysis of fish tissue and water samples.

Quality Control

Laboratory Quality Control

Laboratory quality control procedures as described in Ecology (2000) will include various analyses to evaluate data that are generated. For water samples, check standards will be used to estimate analytical accuracy and bias. The standard deviation of the check standard results gives one estimate of analytical precision. Bias can be estimated by finding the difference between the mean of the check standard results and the true value of the check standard. Analytical precision may be estimated using laboratory duplicate analyses by finding the Relative Percent Difference (RPD) or Relative Standard Deviation (RSD) of the results. Method blanks for water sample will be analyzed to assess contamination from laboratory procedures.

For water and tissue samples, matrix spikes will be used to indicate the presence of bias due to the sample matrix while spike duplicate results can help estimate analytical precision. The project officer will indicate which samples should be used for matrix spikes. Analyses of organic compounds will include spikes with surrogate compounds in order to help estimate the accuracy, precision, and bias of the results. For tissue analyses, Standard Reference Materials (SRM) will be obtained from the National Institute of Standards and Technology and submitted “blind” to the laboratory as a regular sample.

Field Quality Control

Field quality control procedures will include blank samples and field replicate samples. About 10% of samples will be blanks or field replicates submitted “blind” to the laboratory. Blank samples will be for water samples only. Water free of organic chemicals will be obtained from MEL, transported to the sample site, transferred to sampling device, then transferred from the sampling device to a sample container.

Field replicates will consist of an additional sample taken from the same location at the same time or within three days of the first sample. For fish tissue, a replicate sample will consist of a separate sample of fish tissue obtained from the same area, number of fish, species, and size range that made up the first sample. Replicate water samples will be taken for about 10% of the sites sampled. A replicate water sample will consist of a separate sample collected within four hours of, and in the same manner as, the first sample. The laboratory will be asked to perform their duplicate analysis (split sample) on the first sample of the replicate pair. This will allow separation of sampling variability from analytical variability.

Data Management

Data management for this project will include written and electronic media generated from field and laboratory activities. Field notes and observations will be recorded by hand onto prepared field forms and/or notebooks. Pertinent data collected in field books will be transferred to electronic media using Microsoft Office products (Word, Excel, Access) and ArcView GIS. After entry into electronic media, the electronic data will be reviewed and compared to handwritten data to check and correct data entry errors. After these reviews, pertinent field data will be entered into Ecology's electronic Environmental Information Management (EIM) system. Hardcopy and electronic data not entered into EIM will be retained in a file system maintained by the project officer.

Laboratory analyses of samples generate data recorded in handwritten and electronic formats. These data will be examined by designated laboratory personnel for: quality control, completeness, accuracy, errors, and usefulness. Analytical data generated by MEL will be entered in the EIM system by MEL. Analytical data generated by contract laboratories will be submitted to MEL electronically to facilitate entry into EIM. For tabular data generated by contract laboratories, comma delimited files are the preferred format with Excel spreadsheet format also acceptable. Information obtained from the analytical procedures other than results will be retained in the laboratory's electronic and hardcopy filing systems.

Audits and Reports

Oversight of project components will occur through established practices within Ecology. The laboratories employed for sample analysis participate in audits that include review of laboratory facilities, capabilities, and analytical performance through various federal and state programs (Ecology, 2000). Laboratories will report the analytical results and data quality through a case narrative, typically provided for each batch of samples analyzed by a specific procedure. Annual reports for the project will be produced which:

- Describe the project and methods used.
- Display locations of sampling sites.
- Assess the quality of the data.
- Summarize the data collected and discuss significant findings.
- Recommend follow-up actions.

Data Review, Verification, and Validation

Hard copy and electronic forms of data will be reviewed and examined for errors, omissions, and legibility. Field data will be examined by the field leader prior to leaving the sampling site. Laboratory data are reviewed by qualified staff at MEL before they are entered into the EIM system and released to the project officer. Where errors or omissions in the data are found, the source of the data (e.g. field sampling personnel, laboratory technician) will be consulted to determine the correct value or form of the data in question. Corrections or qualifications will be made where possible.

Data verification will be determined by examining the quality control information for each set of data. The project officer will examine field data while qualified laboratory staff will examine laboratory data and document findings in a case narrative. Laboratory staff may be consulted in order to review QC data that are normally retained by MEL. The project officer will be responsible for validating all data by examining the complete data record and determining whether the methods and procedures described in this QAPP were used. Results from the quality control procedures used in the laboratory and field will be used to determine how well the data comply with the Measurement Quality Objectives (accuracy, precision, bias) described in Appendix D.

Data Quality Assessment

Data quality assessment is the determination of whether or not the data generated by the project can be used to meet project objectives. The project officer will make this determination by examining the data and quality control information associated with it. The procedures described in the above sections will guide the project officer in making this determination. Others may be consulted where their expertise can be of value (e.g. quality assurance staff, laboratory staff). The project's annual report will discuss data quality and the determination of whether or not the data can be used to meet project objectives. Limitations of the data, where present, will also be described.

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Appendices

Appendix A-1. Candidate Sites and Target Analytes for Fish Tissue Sampling (2001 selections in bold).											
Candidate Sites (alternate sites indented)	Federal Permit Needed?	2001 Selection	Rationale for Selection	Region	Hg	OC Pest	PCBs	PBDEs	Dioxins	Potential Dioxin Source	Comment
Spokane River	No	Yes	urban/industrial; no dioxin data	ERO	0	0	0	0	1	urban area, industry	historical work covers pest/PCBs
Liberty Lake	No	Yes	suburban, ~5mi east of Spokane industrial area	ERO	1	1	1	1	1	urban/rural area, industry	
Colville River	No		ag, mineral industries; Colville Post Poles woodtreating; BPA Colville Substation; Northwest Alloys ore processing/smelter	ERO	1	1	1	1	1	Colville Post Poles Inc; BPA Colville Substation	
Deep Lake, 20mi NE of Colville	No		mining,	ERO	1	0	0	0	0		what metals mined?
Black Lake	No	Yes	reference, small basin, ~ 12mi E of Colville	ERO	1	1	1	1	0		public fishing and boat access
Bayley Lake	No		reference, small basin, ~ 10mi N of Chewelah	ERO	1	1	1	1	0		public fishing and boat access
McDowell Lake	No		reference, small basin, ~ 14mi N of Chewelah	ERO	1	1	1	1	0		public fishing and boat access
Fan lake	No		reference, small basin, ~ 7mi NW of Deer Park	ERO	1	1	1	1	0		public fishing and boat access
Banks Lake	No	Yes	ag, BPA maint facilities, power generation	CRO	1	1	1	1	1	Lake Roosevelt water	popular lake
Entiat River	Yes		whole sucker fish had hi DDT; no sportfish collected; WSPMP94 suspects fillets would exceed human health criteria; ag sources	CRO	1	1	1	1	0		WSPMP94
Columbia River, Brewster to Pateros	Yes		ag, orchard, pesticide dump, Brewster STP	CRO	1	1	1	1	1	Lake Roosevelt water	
Billy Clapp Lake	No		poss. Reference, bordered by wildlife area; ~ 18mi	CRO	1	1	1	1	0	surface water from S. Banks Lake	public fishing and boat access
Blue Lake	No		poss. reference, State Park area; ~17mi N of Ephr	CRO	1	1	1	1	0	seep water from S. Banks Lake	public fishing and boat access
North Lake, Federal Way	No	Yes	urban, downwind of industrial, Asarco	NWRO	1	1	1	1	1	urban area, industry, Tacoma tideflats/Asarco	
Lake Dolloff, Federal Way	Maybe		urban, downwind of industrial, Asarco	NWRO	1	1	1	1	1	urban area, industry, Tacoma tideflats/Asarco	
Lake Fenwick, Federal Way	No		urban, downwind of industrial, Asarco	NWRO	1	1	1	1	1	urban area, industry, Tacoma tideflats/Asarco	
Steele Lake, Federal Way	No		urban, downwind of industrial, Asarco	NWRO	1	1	1	1	1	urban area, industry, Tacoma tideflats/Asarco	
Lake Desire, E of Federal Way	No		urban, industry; poss Asarco influence; E of SeaTac	NWRO	1	1	1	1	1	urban area, industry, Tacoma tideflats/Asarco	
Five Mile Lake Park, SE of Federal Way	No		near Algona, urban, downwind of industrial, Asarco	NWRO	1	1	1	1	1	urban area, industry, Tacoma tideflats/Asarco	
Panther Lake, SeaTac	No		urban, downwind of industrial, Asarco	NWRO	1	1	1	1	1	urban area, industry, Tacoma tideflats/Asarco	
Angle Lake Park, SeaTac	No		urban, SeaTac air traffic; downwind of industrial, Asarco	NWRO	1	1	1	1	1	urban area, industry, Tacoma tideflats/Asarco	
Snake Lake, Tacoma	No		urban, industry; poss Asarco influence	SWRO	1	1	1	1	1	urban area, industry	public fishing?
Green Lake, Seattle	No	Yes	dense urban; dry cleaners, gas stations, maint shops, radiator shop	NWRO	1	1	1	1	1	urban area, industry	
Meridian Lake, Kent	No		urban, dense shoreline development	NWRO	1	1	1	1	1	urban area	
Mercer Slough	Yes		WSPMP92 pesticides in whole bottom fish, no fillet data	NWRO	1	1	1	1	1		WSPMP92 and later
Lake Union, Seattle	Yes		urban; contaminated sediments;	NWRO	1	1	1	1	1	urban area, industry	
Lake Ballinger, Edmonds	Maybe		urban, Lynwood Safety-Kleen; other industry; PAHs in USGS sed core study	NWRO	1	1	1	1	1	urban area, industry	USGS sed core study
Lake Stevens, E of Everett	Maybe		~ 5mi E of Everett; Weyco and Kimberly Clark pulp mills; suburban/rural area	NWRO	1	1	1	1	1	pulp mills, urban	
Lake Terrell	Yes (WDFW provide fish)	Yes	rural, ag; NWRO interest re Hg, PCBs; Intalco; Arco & Tosco refineries; Ferndale incinerator, all nearby	NWRO	1	1	1	1	1	Arco - Tosco refineries;Intalco; Ferndale incinerator	WDFW collect?
Fazon Lake	No	Yes	rural, ag; NWRO interest re Hg, PCBs, ~ 15mi E of industrial areas near Lake Terrell	NWRO	1	0	0	0	0	Arco - Tosco refineries;Intalco; Ferndale incinerator; Bellingham	WDFW collect?
Wiser Lake	Yes (WDFW provide fish)	Yes	rural, ag; NWRO interest re Hg, PCBs, ~ 15mi E of industrial areas near Lake Terrell	NWRO	1	0	0	0	0	Arco - Tosco refineries;Intalco; Ferndale incinerator, Bellingham	WDFW collect?

Appendix A-1. Candidate Sites and Target Analytes for Fish Tissue Sampling (2001 selections in bold).											
Candidate Sites (alternate sites indented)	Federal Permit Needed?	2001 Selection	Rationale for Selection	Region	Hg	OC Pest	PCBs	PBDEs	Dioxins	Potential Dioxin Source	Comment
Samish Lake	Yes (WDFW provide fish)	Yes	rural; NWRO interest re Hg, PCBs; part of 10Lakes89 study - higher levels of arsenic and PAHs in sed	NWRO	1	0	0	0	0	Bellingham urban area, WDFW collect	public fishing? WDFW collect? 10Lakes89
Lake Padden	Yes (WDFW provide fish)	Yes	suburban, edge of Bellingham, close to Lake Whatcom	NWRO	1	0	0	0	0	urban area, pulp mill, industry	
Lake River	Yes		WSPMP92 no fillet data, whole fish only for several pesticides; Pacific Wood Treating; Ridgefield STP; urban area	SWRO	1	1	1	1	1	Pacific Wood Treating	WSPMP92
Silver Lake	Yes		8 mi NE of Longview;pulp mills; aluminum smelters; Weyco camp HQ in basin	SWRO	1	1	1	1	1	urban area, pulp mills	no historical work
Lacamas Lake	Yes		edge of urban area (Vancouver, Portland); Fort James Specialty Chemical; James River pulp; smelter and chemical plants to west	SWRO	1	1	1	1	1	urban & industrial areas, pulp mill	
Mayfield Lake	No		far downwind of Centralia steam plant	SWRO	1	1	1	1	1	Chehalis coal plant	popular lake
McIntosh Lake	No	Yes	Tenino area, downwind of Centralia steam plant	SWRO	1	0	0	0	1	Chehalis coal plant	
Offut Lake, N of Tenino	Maybe		downwind of Centralia steam plant	SWRO	1	0	0	0	1	Chehalis coal plant	access?
Clear Lake, 10 mi SE Vail	No		downwind of Centralia coal-fired power plant	SWRO	1	0	0	0	1	Chehalis coal plant	public fishing?
Lake Lawrence, Vail	Maybe		downwind of Centralia steam plant	SWRO	1	0	0	0	1	Chehalis coal plant	public fishing?
Harts Lake, SE of McKenna	Maybe		downwind of Centralia steam plant	SWRO	1	0	0	0	1	Chehalis coal plant	restricted launch
Lake Devereaux	No		small drainage, sparse rural; ~ 3mi S of Belfair	SWRO	1	1	1	1	0		public fishing and boat access
Mission Lake	No		small drainage, sparse rural; ~ 5mi N of Belfair	NWRO	1	1	1	1	0		public fishing and boat access
Benson Lake	No		small drainage, sparse rural; ~ 9mi SW of Belfair	SWRO	1	1	1	1	0		public fishing and boat access
2nd species at primary sites as available		Yes			# analyses ---->	5	10	10	10	0	
<i>Sample numbers and cost estimation</i>											
					# analyses ---->	16	16	16	16	7	
					cost/analysis ---->	\$51		\$507		\$1,250	
					subtotal cost ---->	\$816		\$8,112		\$8,750	

Appendix A-2. Candidate Sites and Target Analytes for Water Sampling: Initial Year.

Candidate Sites	Rationale for Selection	Region	OC Pest	Pesticide Screen	Long dd	Lat dd
Fall 2001						
Banks Lake	concurrent with fish collection	CRO	1		119.0320	47.9391
Green Lake, Seattle	concurrent with fish collection	NWRO	1		122.3377	47.6782
Liberty Lake	concurrent with fish collection	ERO	1		117.0775	47.6447
Lake Terrell	concurrent with fish collection	NWRO	1		122.6878	48.8658
North Lake, Federal Way	concurrent with fish collection	NWRO	1		122.2880	47.3058
Black Lake	concurrent with fish collection	ERO	1		117.6253	48.5609
Spring/Summer 2002						
<u>WSPMP sites recommended for long term monitoring</u>						
Mission Creek at Mission Creek Rd	ag - orchard (sampled in '92, '93, and '94)	CRO		1	120.4718	47.5121
Mercer Creek at mouth	urban (sampled in '92, '93, and '94)	NWRO		1	122.1828	47.6017
Moxee Drain at mouth	ag - row crop& orchard (sampled in '92 and '93)	CRO		1	120.4610	46.5413
<u>Lower Wenatchee River tribs</u>	WSPMP recommended more monitoring in area	CRO		3	3 sites to be determined	
<u>Northern Puget Sound</u>						
California Creek near Blaine	ag/rural	NWRO		1	122.7316	48.9623
Terrell Creek near mouth	ag/rural/industry	NWRO		1	122.7441	48.9173
Gages Slough near Burlington	ag	NWRO		1	122.3591	48.4498
<u>Vancouver area</u>						
Burnt Bridge Creek near mouth	urban	SWRO		1	122.6722	45.6631
China Ditch near mouth	rural/ag	SWRO		1	122.4938	45.6938
Lacamas Creek at Goodwin Rd.	rural/ag	SWRO		1	122.4556	45.6390
<u>Sequim area</u>						
Matriotti Creek near mouth	ag/rural	SWRO		1	123.1471	48.1361
Meadowbrook Creek	ag/rural	SWRO		1	123.1238	48.1513
<u>Western Coast</u>						
Ocean Shores canal	rura/rurban homes fronting canal	SWRO		1	124.1485	46.9463
Calawah River near Forks	rural/national forest	SWRO		1	124.4319	47.9477
Fry Creek in Aberdeen	urban	SWRO		1	123.8499	46.9701
<u>Long Beach Peninsula</u>						
113th St. drain near mouth	ag/rural	SWRO		1	124.0178	46.3854
Tarlatt Slough near mouth	ag/rural	SWRO		1	124.0162	46.3718
Holman Rd. drain near mouth	ag/rural	SWRO		1	124.0596	46.3305
<u>Spokane / Deer Park area</u>						
Hangman Creek at Hatch Rd.	ag	ERO		1	117.4011	47.5878
Hangman Creek near Waverly	ag	ERO		1	117.2466	47.3517
Dragoon Creek at Cresent Rd.	ag/rural	ERO		1	117.3729	47.8764
Little Deep Creek at Shady Slope Rd.	ag/rural	ERO		1	117.3771	47.7974
Deadman Creek at Shady Slope Rd.	ag/rural	ERO		1	117.3758	47.7935
Little Spokane River at Rutter Parkway	ag/rural	ERO		1	117.4945	47.7811

Appendix B. Target Analytes for Tissue and Water Samples.

Analyte	Water	Tissue	note	Analyte	Water	Tissue	note
Chlorinated Pesticides, PCBs, PBDEs (note from MEL User's Manual: s = surrogate; 1 = by request only)							
2,4'-DDD	x	x		Endrin	x	x	
2,4'-DDE	x	x		Endrin Aldehyde	x	x	
2,4'-DDT	x	x		Endrin Ketone	x	x	
4,4'-DDD	x	x		gamma-BHC (Lindane)	x	x	
4,4'-DDE	x	x		gamma-Chlordene	x	x	
4,4'-DDT	x	x		Heptachlor	x	x	
4,4-Dibromooctafluorobiphenyl (DBOB)	x	x	s	Heptachlor Epoxide	x	x	
4,4'-Dichlorobenzophenone+A13	x	x	1	Hexachlorobenzene	x	x	
Aldrin	x	x		Kelthane	x	x	
alpha-BHC	x	x		Methoxychlor	x	x	
alpha-Chlordene	x	x		Mirex	x	x	
beta-BHC	x	x		Oxychlordane	x	x	
Caprolactam	x	x	1	Pentachloroanisole	x	x	1
Captafol	x	x	1	Tetrachloro-m-xylene (TCMX)	x	x	s
Captan	x	x	1	Tetradifon (Tedion)	x	x	1
Chlorbenseide	x	x	1	Toxaphene	x	x	
Chlordane (Tech)	x	x		trans-Chlordane (gamma)	x	x	
cis-Chlordane (alpha-Chlordane)	x	x		trans-Nonachlor	x	x	
cis-Nonachlor	x	x		PCB-1221		x	
Dacthal (DCPA)	x	x	1	PCB-1232		x	
DDMU	x	x		PCB-1242		x	
Decachlorobiphenyl (DCB)	x	x	s	PCB-1248		x	
delta-BHC	x	x		PCB-1254		x	
Dibutylchloredate (DBC)	x	x	s	PCB-1260		x	
Dieldrin	x	x		2,2',4,4'-TBDE		x	
Endosulfan I	x	x		2,2',4,4',6-PeBDE		x	
Endosulfan II	x	x		2,2',4,4',5-PeBDE		x	
Endosulfan Sulfate	x	x		2,2',4,4',5,6'-HxBDE		x	
				2,2',4,4',5,5'-HxBDE		x	
PCDD/PCDFs							
2,3,7,8-TCDD		x		2,3,4,7,8-PeCDF		x	
1,2,3,7,8-PeCDD		x		1,2,3,4,7,8-HxCDF		x	
1,2,3,4,7,8-HxCDD		x		1,2,3,6,7,8-HxCDF		x	
1,2,3,6,7,8-HxCDD		x		2,3,4,6,7,8-HxCDF		x	
1,2,3,7,8,9-HxCDD		x		1,2,3,7,8,9-HxCDF		x	
1,2,3,4,6,7,8-HpCDD		x		1,2,3,4,6,7,8-HpCDF		x	
1,2,3,4,6,7,8,9-OCDD		x		1,2,3,4,7,8,9-HpCDF		x	
2,3,7,8-TCDF		x		1,2,3,4,6,7,8,9-OCDF		x	
1,2,3,7,8-PeCDF		x					
Metals							
Mercury		x					
Pesticides Screen (during pesticide application season only)							
2,4'-DDD	x			Coumaphos	x		
2,4'-DDE	x			Cyanazine	x		
2,4'-DDT	x			Cycloate	x		
4,4'-DDD	x			DDMU	x		
4,4'-DDE	x			Decachlorobiphenyl	x		
4,4'-DDT	x			delta-BHC	x		
Abate (Temephos)	x			Demeton-O	x		
Alachlor	x			Demeton-S	x		
Aldrin	x			Di-allate (Avadex)	x		

Appendix B. Target Analytes for Tissue and Water Samples.

Analyte	Water	Tissue	note	Analyte	Water	Tissue	note
alpha-BHC	x			Diazinon	x		
alpha-Chlordene	x			Dichlorvos (DDVP)	x		
Ametryn	x			Dieldrin	x		
Atraton	x			Diethyl Fumarate	x		
Atrazine	x			Dimethoate	x		
Azinphos (Guthion)	x			Dimethylnitrobenzene	x		
Benefin	x			Dioxathion	x		
beta-BHC	x			Diphenamid	x		
Bolstar (Sulprofos)	x			Disulfoton (Di-Syston)	x		
Bromacil	x			Diuron	x		
Butachlor	x			Endosulfan I	x		
Butifos (DEF)	x			Endosulfan II	x		
Butylate	x			Endrin Ketone	x		
Captafol	x			EPN	x		
Captan	x			Eptam	x		
Carbophenothion	x			Ethalfuralin (Sonalan)	x		
Carboxin	x			Ethion	x		
Chlorothalonil (Daconil)	x			Ethoprop	x		
Chlorpropham	x			Ethyl Azinphos (Ethyl Guthion)	x		
cis-Chlordane (alpha-Chlordane)	x			Fenamiphos	x		
				Fenarimol	x		
Fenitrothion	x			Parathion	x		
Fensulfothion	x			Pebulate	x		
Fenthion	x			Pendimethalin	x		
Fenvalerate (2 isomers)	x			Phenothrin	x		
Fluridone	x			Phorate	x		
Fonofos	x			Phosphamidan	x		
gamma-BHC (Lindane)	x			Profluralin	x		
gamma-Chlordene	x			Prometon (Pramitol 5p)	x		
Heptachlor	x			Prometryn	x		
Heptachlor Epoxide	x			Pronamide (Kerb)	x		
Hexazinone	x			Propachlor (Ramrod)	x		
Imidan	x			Propargite	x		
Kelthane	x			Propazine	x		
Malathion	x			Propetamphos	x		
Merphos (1 & 2)	x			Resmethrin	x		
Metalaxyl	x			Ronnel	x		
Methoxychlor	x			Simazine	x		
Methyl Chlorpyrifos	x			Sulfotepp	x		
Methyl Paraoxon	x			Tebuthiuron	x		
Methyl Parathion	x			Terbacil	x		
Metolachlor	x			Terbutryn (Igran)	x		
Metribuzin	x			Tetrachlorvinphos (Gardona)	x		
Mevinphos	x			Tetraethyl Pyrophosphate	x		
MGK264	x			trans-Chlordane (gamma)	x		
Mirex	x			trans-Nonachlor	x		
Molinate	x			Treflan (Trifluralin)	x		
Monocrotophos	x			Triadimefon	x		
Napropamide	x			Triallate	x		
Norflurazon	x			Triphenyl Phosphate	x		
Oxychlordane	x			Vernolate	x		
Oxyfluorfen	x			unknown heteroatom containing compounds; chromato- graphable and extractable.			
					x		

Appendix C. Target Fish Species for Toxics Monitoring Program.

Family name	Common name	Scientific name	Primary Analytes	Spawning Period	Spawning temperature (F)
<u>Predator/Gamefish species</u>					
Salmonidae	Rainbow trout*	<i>Oncorhynchus mykiss</i>	organics	Feb-Jun; also fall spawners	-
Salmonidae	Mountain Whitefish	<i>Prosopium williamsoni</i>	organics	Oct-Dec	-
Salmonidae	Lake Whitefish	<i>Coregonus clupeaformis</i>	organics	Oct-Jan	-
Salmonidae	Cutthroat trout **	<i>Oncorhynchus clarki</i>	organics	Apr-May (inland stock); Dec-Feb (sea run stock)	-
Salmonidae	Kokanee salmon	<i>Oncorhynchus nerka</i>	organics	Sep-Dec	-
Salmonidae	Brown trout	<i>Salmo trutta</i>	organics	Oct-Dec	-
Salmonidae	Lake trout	<i>Salvelinus namaycush</i>	organics	Oct-Dec	-
Salmonidae	Brook trout	<i>Salvelinus fontinalis</i>	organics	Aug - Dec	40 - 50
Centrarchidae	Largemouth bass	<i>Micropterus salmoides</i>	mercury	May-Jul	-
Centrarchidae	Smallmouth bass	<i>Micropterus dolomieu</i>	mercury	May-Jul	55 - 65
Centrarchidae	Black crappie	<i>Pomoxis nigromaculatus</i>	mercury	May-Jun	58 - 64
Centrarchidae	White crappie	<i>Pomoxis annularis</i>	mercury	Spring	64 - 68
Percidae	Yellow perch	<i>Perca flavescens</i>	mercury	Apr-May	45 - 52
Percidae	Walleye	<i>Stizostedion vitreum</i>	mercury	Early spring	38 - 44
<u>Bottom-dwelling species</u>					
Cyprinidae	Common carp	<i>Cyprinus carpio</i>	organics and mercury	Spring-summer	60 - 85
Ictaluridae	Channel catfish	<i>Ictalurus punctatus</i>	organics and mercury	Spring	70 - 80
Ictaluridae	Brown bullhead	<i>Ictalurus nebulosus</i>	organics and mercury	Apr-Jun	70+
Catostomidae	Largescale Sucker	<i>Catostomus macrochelius</i>	organics	Apr-May	-
Catostomidae	Longnose Sucker	<i>Catostomus catostomus</i>	organics	Spring, after icemelt	41+
Catostomidae	Bridgeliip Sucker	<i>Catostomus columbianus</i>	organics	May-Jun	-
Acipenseridae	White Sturgeon	<i>Acipenser transmontanus</i>	organics and mercury	May-Jun	48 - 63

Notes:

Bull trout (*Salvelinius confluentes*) throughout WA and the NW listed as Threatened under the ESA. Spawns Aug-Nov.

* Steelhead from Lower, Middle, Upper Columbia River and Snake River basins listed as Endangered or Threatened under the ESA.

** Coastal cutthroat trout (SW WA and Columbia River) proposed for ESA listing.

Appendix D. Measurement Quality Objectives.

Parameter	Matrix	Practical Quantitation Limit*	Bias (as % of true value)	Overall Precision (as RSD of field duplicate)	Accuracy** (as % deviation from true value)
Mercury (total)	tissue	0.005 mg/kg, wet	25	14	53
Chlorinated pesticides & PCBs & PBDEs	tissue	0.25-15 ug/kg, wet	50	28	107
PCDD/PCDFs (17 congeners)	tissue	0.1 - 1.0 ng/kg, wet	25	28	82
Lipids - percent	tissue	0.1%	10	14	38
Chlorinated pesticides	water	0.01 - 0.1 ug/L	50	28	107
Pesticide Screen - Cl,Br,I,N,S,Ps + TICs	water	0.01 - 0.1 ug/L	50	28	107
TOC	water	1 mg/L	5	10	25
TSS	water	1 mg/L	5	10	25

* Where range is given, the PQL varies among individual compounds in the analytical group

** Accuracy = Bias + Precision (precision expressed as 2*RSD)

Appendix E. Field Procedures for Fish Collection and Packaging for Transport.

Fish will be collected for measuring contaminant levels in fillets from legal size fish. Larger fish are preferred due to their likelihood of bioaccumulating contaminants of interest. See Appendix D for the list of target species. Contact the regional WDFW biologist for information about the species available at the sampling site.

Ten fish are needed for making a composite sample. If ten are not available, get as many as possible with the minimum being five fish. The length of the smallest fish should be no less than 75% of the length of the largest fish.

Since specimens will be analyzed for low-level chemical residues, there are a number of precautions that should be taken when handling them. They are as follows:

1. Once captured, consider how fish might get contaminated while in the field. At some sites, fish may need to go into plastic trash bags lining a five-gallon bucket. The live well in the electrofishing boat may be used if contamination is unlikely.
2. At the close of the day's fishing effort, process the fish for transport and short-term storage. Begin by recording the species, total length, and weight of individual fish; note any observations about individual fish.
3. Wrap each fish individually in two layers of aluminum foil (dull side in). In between layers, place a sample tag containing the date, site, species, ID number, and who collected.
4. Put fish in large zip-lock bags. Don't mix species in the zip-locks. Use a Sharpie to label the exterior of the bag with the date, site, and species, and fish ID numbers.
5. Place bagged samples on ice as soon as possible. Drain any ice water that builds up in the cooler to prevent contamination.
6. Samples should be frozen to -20 C upon return from the field; preferably within 24 hours of collection. A 48 hour period is acceptable if ice and cooling are carefully managed. Fish tissue will be processed for laboratory analyses at a later date.

Appendix F. Summary of Analytical Methods, Quantitation Limits, Containers, and Holding Times for Target Analytes.

Parameter	Matrix	Description	Method	Practical Quantitation Limit	Sample Container	Preservation	Holding Time
Mercury	tissue	CVAA	EPA 245.5; MEL SOP*	0.005 mg/kg, wet	precleaned glass jar w/teflon lid, 2 oz	-20 C	28 days
Chlorinated pesticides	tissue	GC/ECD	EPA 8081; MEL SOP*	0.25 - 15 ug/kg, wet	precleaned glass jar w/teflon lid, 2 oz	-20 C	1 year
PCBs & PBDEs	tissue	GC/ECD	EPA 8082; MEL SOP*	0.25 ug/kg, wet	precleaned glass jar w/teflon lid, 2 oz	-20 C	1 year
PCDD/PCDFs (17 congeners)	tissue	HiRes GC/MS	EPA 1613B	0.1 - 1.0 ng/kg, wet	precleaned glass jar w/teflon lid, 2 oz	-20 C	1 year
Lipids - percent	tissue	gravimetric	EPA 608.5	0.1%	taken from pesticide tissue sample	-20 C	1 year
Chlorinated pesticides	water	GC/ECD	EPA 8081; MEL SOP*	0.01 ug/L	precleaned glass jar w/teflon lid, 1 gallon	4 C	7 days
Pesticide Screen - Cl,Br,I,N,S,Ps + TICs	water	GC/AED	EPA 8085; MEL SOP*	0.01 - 0.1 ug/L	precleaned glass jar w/teflon lid, 1 gallon	4 C	7 days
TOC	water	Combustion NDIR	EPA 415.1	1 mg/L	60 mL PE bottle	4 C, H2SO4 to pH <2	28 days
TSS	water	gravimetric	EPA 160.2	1 mg/L	1 L PE bottle	4 C	7 days

* MEL modifications to analytical methods are documented in their Standard Operating Procedures:

EPA 245.5: "Standard Operating Procedure for the Determination of Mercury by Cold Vapor Atomic Absorbance in Sediments US EPA SW846 7471B Modified, and 245.5, Modified (Sediment)." (also used for tissue)

EPA 8081 and EPA 8082 - SOP # 730002: Analysis of Water/Soil/Sediment/Fish Tissue Samples for Organochlorine Pesticides, Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls by GC/ECD

EPA 8085 - SOP # 730001: Pesticides Screening and Compound Independent Elemental Quantitation by Gas Chromatography with Atomic Emission Detection (AED), Method 8085

Appendix G. Target Analytes and Practical Quantitation Limits (PQL) for Tissue and Water Samples.

Note: **bold** values may not be achievable

Analyte	PQL Water (ug/L)	PQL Tissue (ug/Kg wet)	note	Analyte	note	PQL Water (ug/L)	PQL Tissue (ug/Kg wet)
Chlorinated Pesticides, PCBs, PBDEs (note from MEL User's Manual: s = surrogate; 1 = by request only)							
2,4'-DDD	0.001	0.25		Endrin		0.002	0.50
2,4'-DDE	0.001	0.25		Endrin Aldehyde		0.01	0.50
2,4'-DDT	0.001	0.25		Endrin Ketone		0.01	0.50
4,4'-DDD	0.001	0.25		gamma-BHC (Lindane)		0.01	0.25
4,4'-DDE	0.001	0.25		gamma-Chlordene		0.01	0.25
4,4'-DDT	0.001	0.25		Heptachlor		0.003	0.25
4,4-Dibromooctafluorobiphenyl (DBOB)	0.01	0.25	s	Heptachlor Epoxide		0.003	0.25
4,4'-Dichlorobenzophenone1	0.01	0.25	1	Hexachlorobenzene		0.01	0.25
Aldrin	0.001	0.25		Kelthane		0.01	0.50
alpha-BHC	0.01	0.25		Methoxychlor		0.01	0.50
alpha-Chlordene	0.01	0.25		Mirex		0.01	0.50
beta-BHC	0.01	0.25		Oxychlordane		0.01	0.25
Caprolactam	0.01	0.25	1	Pentachloroanisole	1	0.01	0.25
Captafol	0.01	0.25	1	Tetrachloro-m-xylene (TCMX)	s	0.01	0.25
Captan	0.01	0.25	1	Tetradifon (Tedion)	1	0.01	2.0
Chlorbenside	0.01	0.25	1	Toxaphene		0.0002	9.8
Chlordane (Tech)	0.001	0.25		trans-Chlordane (gamma)		0.001	0.25
cis-Chlordane (alpha-Chlordane)	0.001	0.25		trans-Nonachlor		0.001	0.25
cis-Nonachlor	0.001	0.25		PCB-1221		n/a	1.0
Dacthal (DCPA)	0.01	0.25	1	PCB-1232		n/a	1.0
DDMU	0.01	0.25		PCB-1242		n/a	1.0
Decachlorobiphenyl (DCB)	0.01	0.25	s	PCB-1248		n/a	1.0
delta-BHC	0.01	0.25		PCB-1254		n/a	1.0
Dibutylchloroendate (DBC)	0.01	0.25	s	PCB-1260		n/a	1.0
Dieldrin	0.001	0.50		2,2',4,4'-TBDE		n/a	2.5
Endosulfan I	0.01	0.50		2,2',4,4',6-PeBDE		n/a	2.5
Endosulfan II	0.01	0.50		2,2',4,4',5-PeBDE		n/a	2.5
Endosulfan Sulfate	0.01	0.50		2,2',4,4',5,6'-HxBDE		n/a	2.5
				2,2',4,4',5,5'-HxBDE		n/a	2.5
PCDD/PCDFs							
2,3,7,8-TCDD	n/a	0.00005		2,3,4,7,8-PeCDF		n/a	0.00005
1,2,3,7,8-PeCDD	n/a	0.00005		1,2,3,4,7,8-HxCDF		n/a	0.00005
1,2,3,4,7,8-HxCDD	n/a	0.00005		1,2,3,6,7,8-HxCDF		n/a	0.00005
1,2,3,6,7,8-HxCDD	n/a	0.00005		2,3,4,6,7,8-HxCDF		n/a	0.00005
1,2,3,7,8,9-HxCDD	n/a	0.00005		1,2,3,7,8,9-HxCDF		n/a	0.00005
1,2,3,4,6,7,8-HpCDD	n/a	0.00005		1,2,3,4,6,7,8-HpCDF		n/a	0.00005
1,2,3,4,6,7,8,9-OCDD	n/a	0.00005		1,2,3,4,7,8,9-HpCDF		n/a	0.00005
2,3,7,8-TCDF	n/a	0.00005		1,2,3,4,6,7,8,9-OCDF		n/a	0.00005
1,2,3,7,8-PeCDF	n/a	0.00005					
Metals							
Mercury	n/a	5					
Pesticides Screen (during pesticide application season only)							
2,4'-DDD	0.001	n/a		Coumaphos		0.01	n/a
2,4'-DDE	0.001	n/a		Cyanazine		0.01	n/a
2,4'-DDT	0.001	n/a		Cycloate		0.01	n/a
4,4'-DDD	0.001	n/a		DDMU		0.01	n/a
4,4'-DDE	0.001	n/a		Decachlorobiphenyl		0.01	n/a
4,4'-DDT	0.001	n/a		delta-BHC		0.01	n/a
Abate (Temephos)	0.01	n/a		Demeton-O		0.01	n/a
Alachlor	0.01	n/a		Demeton-S		0.01	n/a
Aldrin	0.004	n/a		Di-allate (Avadex)		0.01	n/a
alpha-BHC	0.01	n/a		Diazinon		0.01	n/a
alpha-Chlordene	0.001	n/a		Dichlorvos (DDVP)		0.01	n/a

Appendix G. Target Analytes and Practical Quantitation Limits (PQL) for Tissue and Water Samples.

Note: **bold** values may not be achievable

Analyte	PQL Water (ug/L)	PQL Tissue (ug/Kg wet)	note	Analyte	note	PQL Water (ug/L)	PQL Tissue (ug/Kg wet)
Ametryn	0.01	n/a		Dieldrin		0.004	n/a
Atraton	0.01	n/a		Diethyl Fumarate		0.01	n/a
Atrazine	0.01	n/a		Dimethoate		0.01	n/a
Azinphos (Guthion)	0.01	n/a		Dimethylnitrobenzene		0.01	n/a
Benefin	0.01	n/a		Dioxathion		0.01	n/a
beta-BHC	0.01	n/a		Diphenamid		0.01	n/a
Bolstar (Sulprofos)	0.01	n/a		Disulfoton (Di-Syston)		0.01	n/a
Bromacil	0.01	n/a		Diuron		0.01	n/a
Butachlor	0.01	n/a		Endosulfan I		0.01	n/a
Butifos (DEF)	0.01	n/a		Endosulfan II		0.01	n/a
Butylate	0.01	n/a		Endrin Ketone		0.01	n/a
Captafol	0.01	n/a		EPN		0.01	n/a
Captan	0.01	n/a		Eptam		0.01	n/a
Carbophenothion	0.01	n/a		Ethalfuralin (Sonalan)		0.01	n/a
Carboxin	0.01	n/a		Ethion		0.01	n/a
Chlorothalonil (Daconil)	0.01	n/a		Ethoprop		0.01	n/a
Chlorpropham	0.01	n/a		Ethyl Azinphos (Ethyl Guthion)		0.01	n/a
cis-Chlordane (alpha-Chlordane)	0.001	n/a		Fenamiphos		0.01	n/a
				Fenarimol		0.01	n/a
Fenitrothion	0.01	n/a		Parathion		0.01	n/a
Fensulfothion	0.01	n/a		Pebulate		0.01	n/a
Fenthion	0.01	n/a		Pendimethalin		0.01	n/a
Fenvalerate (2 isomers)	0.01	n/a		Phenothrin		0.01	n/a
Fluridone	0.01	n/a		Phorate		0.01	n/a
Fonofos	0.01	n/a		Phosphamidan		0.01	n/a
gamma-BHC (Lindane)	0.01	n/a		Profluralin		0.01	n/a
gamma-Chlordene	0.001	n/a		Prometon (Pramitol 5p)		0.01	n/a
Heptachlor	0.003	n/a		Prometryn		0.01	n/a
Heptachlor Epoxide	0.003	n/a		Pronamide (Kerb)		0.01	n/a
Hexazinone	0.01	n/a		Propachlor (Ramrod)		0.01	n/a
Imidan	0.01	n/a		Propargite		0.01	n/a
Kelthane	0.01	n/a		Propazine		0.01	n/a
Malathion	0.01	n/a		Propetamphos		0.01	n/a
Merphos (1 & 2)	0.01	n/a		Resmethrin		0.01	n/a
Metalaxyl	0.01	n/a		Ronnel		0.01	n/a
Methoxychlor	0.01	n/a		Simazine		0.01	n/a
Methyl Chlorpyrifos	0.01	n/a		Sulfotepp		0.01	n/a
Methyl Paraoxon	0.01	n/a		Tebuthiuron		0.01	n/a
Methyl Parathion	0.01	n/a		Terbacil		0.01	n/a
Metolachlor	0.01	n/a		Terbutryn (Igran)		0.01	n/a
Metribuzin	0.01	n/a		Tetrachlorvinphos (Gardona)		0.01	n/a
Mevinphos	0.01	n/a		Tetraethyl Pyrophosphate		0.01	n/a
MGK264	0.01	n/a		trans-Chlordane (gamma)		0.001	n/a
Mirex	0.01	n/a		trans-Nonachlor		0.001	n/a
Molinate	0.01	n/a		Treflan (Trifluralin)		0.01	n/a
Monocrotophos	0.01	n/a		Triadimefon		0.01	n/a
Napropamide	0.01	n/a		Triallate		0.01	n/a
Norflurazon	0.01	n/a		Triphenyl Phosphate		0.01	n/a
Oxychlordane	0.001	n/a		Vernolate		0.01	n/a
Oxyfluorfen	0.01	n/a		unknown heteroatom containing compounds; chromato- graphable and extractable.			

Appendix H. Estimated Analytical Costs for the Initial Year of the Toxics Monitoring Program.													
Parameter	Matrix	Cost per sample	No. Samples	QA blank	QA dup	QA MS	QA MSD	QA SRM	Total QA Analyses	Total Cost: Water	Total Cost: Tissue	Cost: QA	
Mercury (total)	tissue	\$ 34	16	0	1	1	1	0	3		\$ 646	\$ 102	
Mercury sample preparation	tissue	\$ 17	16	0	1	1	1	0	3		\$ 323	\$ 51	
Chlorinated pesticides & PCBs & PBDEs	tissue	\$ 507	16	0	1	1	1	1	4		\$ 10,140	\$ 2,028	
PCDD/PCDFs congeners) (17	tissue	\$1,250	7	0	1	0	0	0	1		\$ 10,000	\$ 1,250	
Lipids - percent	tissue	\$ 31	16	0	1	0	0	0	1		\$ 527	\$ 31	
Chlorinated pesticides	water	\$ 225	6	1	1	1	1	0	4	\$ 2,250		\$ 900	
Pesticide Screen - Cl,Br,I,N,S,Ps + TICs	water	\$ 626	24	1	1	1	1	0	4	\$ 17,528		\$ 2,504	
TOC	water	\$ 30	30	0	2	0	0	0	2	\$ 960		\$ 60	
TSS	water	\$ 10	30	0	2	0	0	0	2	\$ 320		\$ 20	
Total Cost/Matrix --->										\$ 21,058	\$ 21,636	\$ 6,946	
TOTAL COST -->										\$ 42,694		(includes QA)	
										water	tissue	total	
QA cost --->										\$ 3,462	\$ 3,484	\$ 6,946	
QA cost as % --->										16%	16%	16%	